α-HYDROPERFLUOROISOPROPYLISOCYANATE

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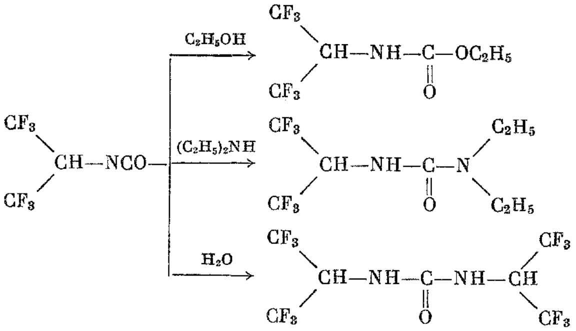
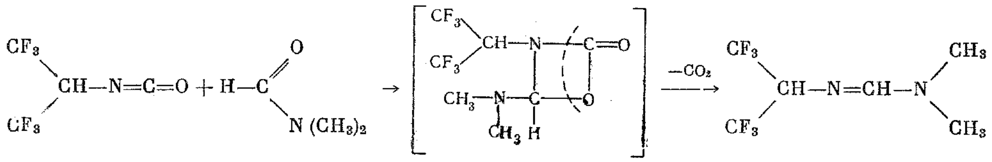
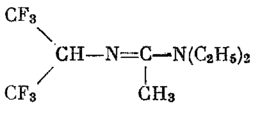
The reaction of perfluoroalkylisocyanates, R_fNCO, with nucleophilic reagents is complicated by the instability of the $-CF_2NH-$ group formed during the reaction [1, 2]. It seemed of interest to study the properties of hexafluoroisopropylisocyanate, $(CF_3)_2CHNCO$, which does not contain a fluorine in the α-position in the $-NCO$ group. The latter compound has not been previously obtained in pure form, although its derivatives have been isolated [3]. We have obtained pure α-hydroperfluoroisopropylisocyanate (I) by decomposing the azide of α-hydrohexafluoroisobutyric acid according to the Curtius reaction, and have shown that it reacts readily with alcohols, amines, and water to form the corresponding urethanes and ureas



One of the characteristic properties of isocyanates is their reaction with N,N-dialkylamides of carboxylic acids, which proceeds with the formation of unstable four-membered rings which decompose and liberate CO_2. Moreover, isocyanates which do not contain fluorine (C_6H_5NCO, for example) react with N,N-dimethylformamide at the boiling point (~ 150°) [4, 5]; sulfonylisocyanates, RSO_2NCO, react at room temperature [6]. Hexafluoroisopropylisocyanate is somewhat less reactive than the sulfonylisocyanates. At room temperature it reacts slowly with dimethylformamide, but at 75-100° it gives N,N-dimethyl-N'-(α-hydroperfluoroisopropyl)formamidine



Analogously, the reaction of hexafluoroisopropylisocyanate with N,N-diethylacetamide gives N,N-diethyl-N'-(α-hydroperfluoroisopropyl)acetamidine



Perfluoroisopropylisocyanate, C_3F_7NCO, reacts with N,N-dimethylformamide on heating, but we did not succeed in isolating the reaction products.

The Staudinger reaction, which leads to the formation of carbodiimides [7-10], is known for nonfluorinated isocyanates. We have studied this reaction with hexafluoroisopropylisocyanate and perfluoro-

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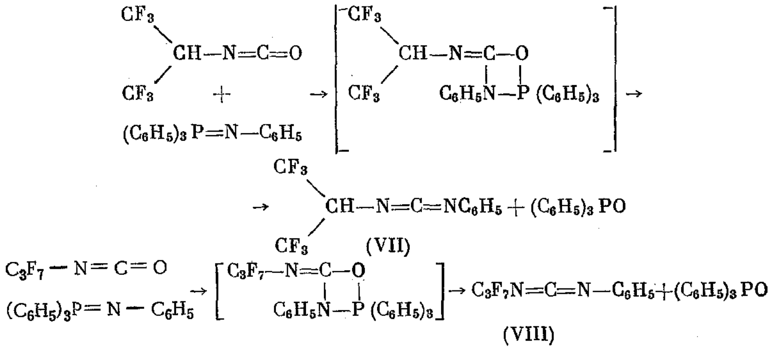
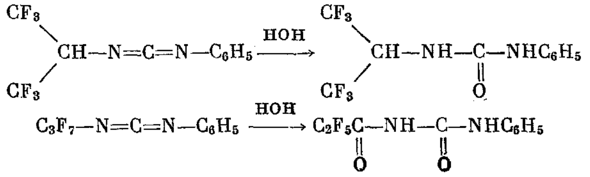
propylisocyanate with the goal of preparing previously unknown fluorine-containing carbodiimides. The reaction of these isocyanates with triphenylphosphinephenylimine under mild conditions yields triphenylphosphine oxide and the fluorine-containing unsymmetrical carbodiimide



The structures of the N-fluoroalkyl-N'-phenylcarbodiimides were confirmed by hydrolysis to the corresponding urea and by infrared spectra



EXPERIMENTAL

α-Hydroperfluoroisopropylisocyanate (I). To a solution of 7.8 g activated NaN_3 in 15 ml water and 20 ml m-xylene was added dropwise, with stirring and cooling, a solution of 21.4 g α-hydroperfluoroisobutyryl chloride in 20 ml m-xylene. The mixture was stirred for an hour in the cold and for 3 h at room temperature. The xylene layer was separated, washed with water, and dried successively over $MgSO_4$ and Na. The dried solution of the azide was heated slowly. At a temperature of ~ 70°, decomposition of the azide with the liberation of nitrogen was observed. The isocyanate was distilled after nitrogen evolution ceased; it was purified by redistillation through a column in a stream of dry nitrogen. The yield of (I) was 11.5 g (59%). The boiling point is 47-49°; n_D^{22} 1.2998. Found %: C 24.63; H 0.67; N 7.04. C_4HF_6NO. Calculated %: C 24.87; H 0.518; N 7.25.

N-(α-Hydroperfluoroisopropyl)ethylurethane (II). An excess of absolute C_2H_5OH was added dropwise with cooling to a solution of 1.93 g (I) in 5 ml absolute ether. The yield of (II) was 2.3 g (98%). The melting point is 63-65° (from C_6H_6). Found %: C 29.74; H 2.69; F 47.62. $C_6H_7F_6NO_2$. Calculated %: C 30.12; H 2.92; F 47.69.

N,N-Diethyl-N'-(α-hydroperfluoroisopropyl) Urea (III). To a solution of 1.93 g (I) in 5 ml absolute ether was added dropwise, with cooling, a solution of 0.73 g diethylamine in 2 ml absolute ether. The yield of (III) was 2.1 g (80%). The melting point is 101-103° (from C_6H_6). Found %: C 36.04; H 4.52; F 42.84. $C_8H_{12}F_6N_2O$. Calculated %: C 36.09; H 4.51; F 42.85.

N,N'-bis-(α-Hydroperfluoroisopropyl) Urea (IV). Several drops of water were added to a solution of 1.93 g (I) in 5 ml dioxane, and the mixture was allowed to stand overnight at room temperature. A yield of 1.2 g (6%) of (IV) was obtained. The melting point is 228-230° (from 50% alcohol). Found %: C 23.33; H 1.10; N 7.75. $C_7H_4F_{12}N_2O$. Calculated %: C 23.33; H 1.11; N 7.77.

N,N-Dialkyl-N'-(α-hydroperfluoroisopropyl)-amidine. A mixture of 3.86 g (I) and 1.46 g absolute N,N-dimethylformamide was heated 3 h at 75° and 4 h at 100° until no more CO_2 evolved. The mixture was dissolved in 20 ml ether and unreacted N,N-dimethylformamide was removed by washing with water. The solution was dried over $MgSO_4$ and the ether distilled off. The residue was vacuum-distilled. Thus was obtained 1.7 g (39%) N,N-dimethyl-(α-hydroperfluoroisopropyl) formamidine (V), with a boiling point of 52-54° (8 mm) and a melting point of 51-53° (from petroleum ether). Found %: C 35.27; H 3.55; F 50.44; N 12.27. $C_6H_8F_6N_2$. Calculated %: C 32.43; H 3.60; F 51.35; N 12.61.

Under analogous conditions, 1.2 g (43%) N,N-diethyl-N'-(α-hydroperfluoroisopropyl)acetamidine (VI) was obtained from 1.93 g (I) and 1.15 g diethylacetamide. Its boiling point is 79-80° (12 mm); n_D^{22} 1.3901. Found %: C 41.42; H 5.56; F 42.29; N 10.52. $C_9H_{14}F_6N_2$. Calculated %: C 40.90; H 5.30; F 43.18; N 10.60.

Carbodiimides. To a solution of 7.1 g triphenylphosphine imine in 15 ml absolute ether at −78° was added 4.1 g (I) or 4.5 g perfluoropropylisocyanate. The mixture was allowed to stand overnight at room temperature in a sealed ampule. The precipitate which appeared (mp 153°) did not give a melting-point depression with a sample of triphenylphosphine oxide. The ether was distilled from the mixture and the residue distilled in vacuum. A yield of 3 g (56%) N-phenyl-N'-(α-hydroperfluoroisopropyl)carbodiimide (VII) was obtained. The boiling point is 76-77° (5 mm); n_D^{22} 1.4553. Found %: C 44.36; H 2.32; N 10.66. $C_{10}H_6F_6N_2$. Calculated %: C 44.77; H 2.23; N 10.44. The infrared spectrum had a very strong band at 2135 cm^{-1} (N=C=N). We also obtained 2.1 g (37%) N-phenyl-N'-perfluoropropylcarbodiimide (VII) from the appropriate reagents. Its boiling point is 72° (7 mm); n_D^{22} 1.4348. Found %: C 41.70; H 1.66; F 46.61; N 9.97. $C_{10}H_5F_7N_2$. Calculated %: C 41.95; H 1.74; F 46.50; N 9.79. The infrared spectrum had a very strong band at 2150 cm^{-1} (N=C=N).

Hydrolysis of the Carbodiimides. The action of water on a dioxane solution of N-phenyl-N-(α-hydroperfluoroisopropyl)carbodiimide at room temperature resulted in a quantitative yield of N-phenyl-N'-(α-hydroperfluoroisopropyl)urea, with a melting point of 214-216° (from 50% alcohol). Found %: C 41.78; H 2.51; F 39.02; N 9.56. $C_{10}H_8F_6N_2O$. Calculated %: C 41.95; H 2.79; F 39.86; N 9.79.

Hydrolysis of N-phenyl-N'-perfluoropropylcarbodiimide under the same conditions yielded N-phenyl-N'-perfluoropropionylurea with a melting point of 145-147° (from 50% alcohol). Found %: C 42.49; H 2.58. $C_{10}F_5H_7N_2O_2$. Calculated %: C 42.55; H 2.48; F 33.68; N 2.92.

CONCLUSIONS

1. α-Hydroperfluoroisopropylisocyanate was synthesized and some of its reactions were studied.
2. Unsymmetrical fluorine-containing carbodiimides were obtained for the first time.

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